[Contribution from the School of Chemistry of the University of Minnesota]

THE ACTION OF DIAZOMETHANE UPON α,β-UNSATURATED KETONES. I. BENZALACETOPHENONE

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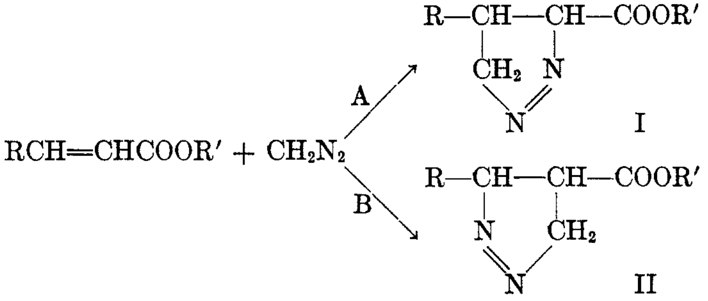
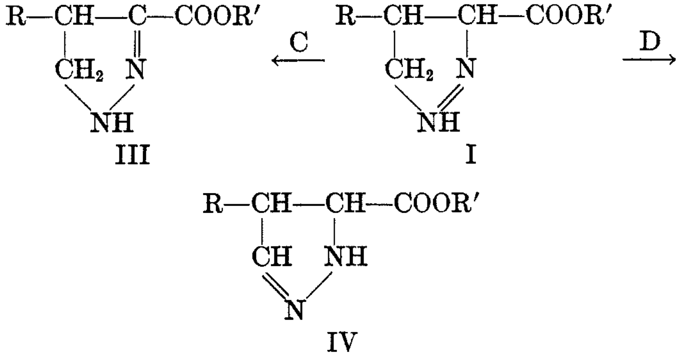
It has been shown by von Auwers[1] that the addition of diazomethane to α,β-unsaturated esters proceeds in such a way that the nitrogen atoms become attached to the α-carbon atom, *i.e.*, the reaction follows scheme A rather than B.



von Auwers (*loc. cit.*) also showed that under the influence of certain reagents (such as halogen acids), the Δ^1-pyrazolines first formed could be changed to the isomeric Δ^2-pyrazolines and that, wherever possible, this change resulted in the formation of a conjugated system (reaction C):



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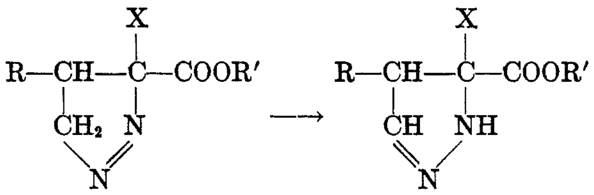
[1] von Auwers, (*a*) *Ann.*, **470,** 284 (1929); (*b*) *ibid.*, **496,**, 27, 252 (1932); (*c*) *Ber.*, **66,** 1198 (1933); see also von Pechmann, (*d*), *Ber.*, **33,** 3590, 3594, 3597 (1900).

However, in the case of substituted pyrazolines, the alternative reaction according to D was found to take place:



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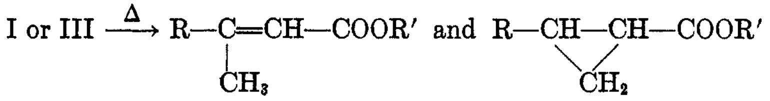
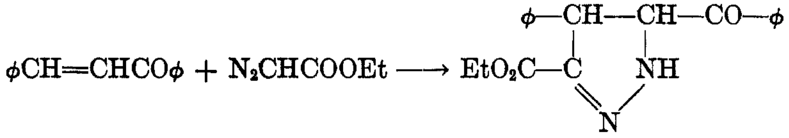
Thermal decomposition of these products led to olefinic esters and cyclopropane derivatives,



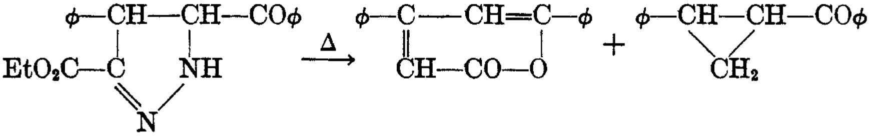
V VI

and the course of this reaction was determined by the complexity of the pyrazoline; the simpler members in general yielding mostly unsaturated compounds.

There is no recorded instance of diazomethane having been added to α,β-unsaturated ketones, but Kohler and Steele[2] in an attempt to prepare substituted cyclopropanes, studied the addition of diazoacetic ester to benzalacetophenone and represented the reaction as taking place in the following manner:



Thermal decomposition of the pyrazoline gave a small yield of the desired cyclopropane, but the reaction led chiefly to the pyrone:



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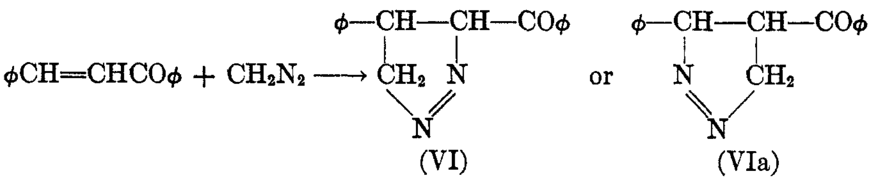
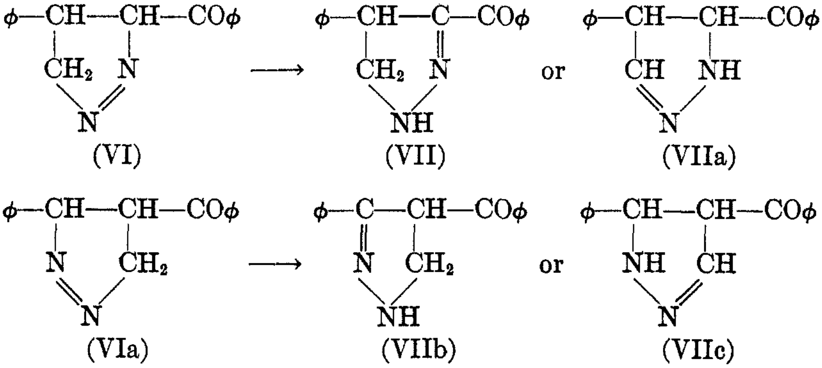
[2] Kohler and Steele, J. Am. Chem. Soc., **41**, 1093 (1919).

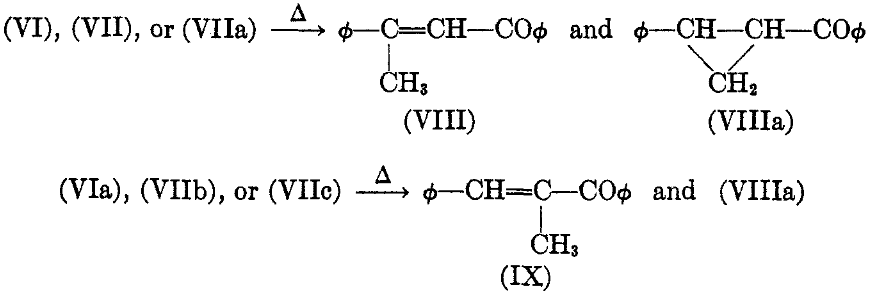
Two modes of addition of diazomethane to benzalacetophenone are structurally possible:



and the change of the Δ^1-pyrazoline primarily formed to the isomeric Δ^2-pyrazoline could then take place according to the following schemes:

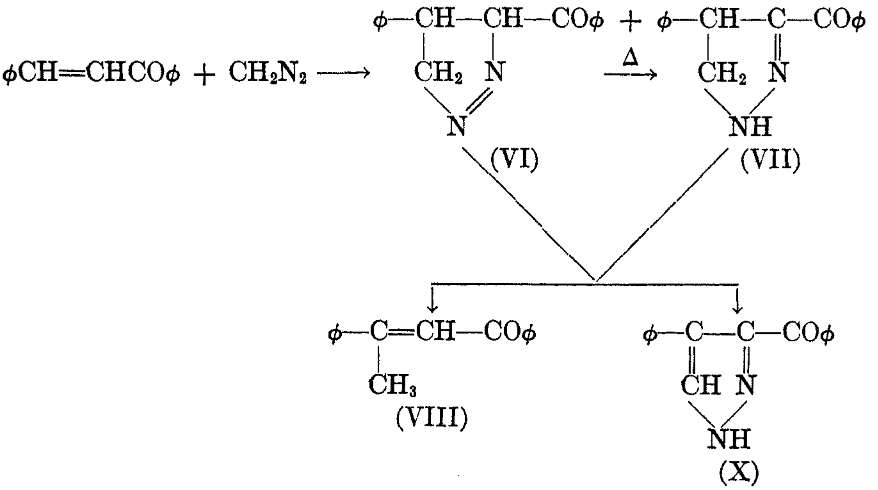


Thermal decomposition of these products should proceed as follows:



In view of the results of von Auwers and Kohler, the primary product to be expected from this reaction is (VI), 3-benzoyl-4-phenyl-Δ^1-pyrazoline, and this was found to be the case. Diazomethane was found to add readily to benzalacetophenone in cold ether solution, giving two isomeric pyrazolines of melting points 92–3° and 127–9°, respectively. The lower-melting product (VI) could be transformed into its isomer (VII) by gentle heating slightly above its melting point. The higher-melting isomer is arbitrarily assigned the structure VII, 3-benzoyl-4-phenyl-Δ^2-pyrazoline, since this structure has a conjugated system (*cf.* von Auwers, *loc. cit.*), although no proof of this formulation has been obtained.

Thermal decomposition of the products was not clean-cut, but in one instance a yellow oil was obtained, which was identified as dypnone (VIII) by the melting point of a mixture of the oxime with dypnone oxime. This shows that the reaction took place in the expected manner, and that the nitrogens are adjacent to the carbonyl group. In another case, the thermal decomposition did not lead to loss of nitrogen, but apparently hydrogen was split off, giving a product represented as (X), 3-benzoyl-4-phenyl-pyrazole. The structure of this product was established by oxidation of 3-benzoyl-4-phenyl-Δ^2-pyrazoline by bromine, which gave the same pyrazole. von Auwers[1b] observed a similar type of reaction in one case. The courses of these reactions are indicated as follows:



The addition of diazomethane appears to be a general reaction of α,β-unsaturated ketones, and further work in this field will be reported in a later paper.

EXPERIMENTAL

Addition of diazomethane to benzalacetophenone. Preparation of 3-benzoyl-4-phenyl-Δ^1-pyrazoline (VI).—To the cold ethereal diazomethane solution prepared from ten grams of nitrosomethylurea (*ca.* 2.8 g. CH_2N_2; 0.067 mole; volume 100 cc.) was added a solution of benzalacetophenone (14.5 g.; 0.07 mole) in 150 cc. of ether. Within five minutes a precipitate formed. After an hour at −14° filtration yielded 13.5 g. of colorless material; m.p. 91–93°. Partial evaporation of the ether gave an additional 3 g. of material; m.p. 78–88°. Final evaporation left 1.0 g. of unchanged benzalacetophenone. The total yield, based on 13.5 g. of benzalacetophenone (0.065 mole), was 100%.

The material may be crystallized from methyl or ethyl alcohol, a mixture of ethyl acetate and petroleum ether, a mixture of chloroform and petroleum ether, or from carbon tetrachloride. The best results were obtained with the use of methyl alcohol. The melting point after two crystallizations was 92–93°.

Anal. Calc'd for $C_{16}H_{14}N_2O$: C, 76.77; H, 5.64; N, 11.20; mol. wt. 2.50
Found: C, 76.56, 76.50; H, 5.85, 5.80; N, 11.35, 11.13; mol. wt. (in benzene), 265, 241, 244.

Upon standing for about four months this material decomposed to an oil, from which no crystalline material could be isolated.

Addition of diazomethane to benzalacetophenone. Preparation of 3-benzoyl-4-phenyl-Δ^1-pyrazoline (VI) and 3-benzoyl-4-phenyl-Δ^2-pyrazoline (VII).—To the cold ethereal diazomethane solution prepared from ten grams of nitrosomethylurea (*ca.* 2.8 g. diazomethane; 0.067 mole; volume 100 cc.) was added a solution of benzalacetophenone (14.5 g.; 0.07 mole) in 150 cc. of dry ether. A colorless precipitate formed in the cold solution within a few minutes. A portion removed and purified melted at 92–3°. The reaction mixture was kept in an ice bath (*ca.* −10°) for one hour, then allowed to come to room temperature slowly. The precipitate appeared to redissolve in part, but after standing and upon shaking, a voluminous precipitate separated. This was separated by filtration, giving 8.5 g. of faintly yellow material. The product may be crystallized from the usual organic solvents; m.p. 127–9°.

Anal. Calc'd for $C_{16}H_{14}N_2O$: C, 76.77; H, 5.64; N, 11.20; mol. wt. 250
Found: C, 76.76; H, 5.89; N, 11.05; mol. wt. (in benzene), 276, 268, 274.

Action of heat on 3-benzoyl-4-phenyl-Δ^1-pyrazoline (VI). Preparation of 3-benzoyl-4-phenyl-Δ^2-pyrazoline (VII).—The pyrazoline (VI) (0.5 g.) was placed in a small test-tube, a thermometer was immersed in the solid, and the tube was heated gently with a small free flame. At 120° there was an apparent reaction, and the temperature rose to 150° without further heating. The temperature was held between 150–170° for 15 minutes; upon cooling and stirring the mass solidified. After crystallization from ethyl alcohol the melting point was 125–129°.

The pyrazoline (VI) (2.0 g.) was placed in a small test-tube and heated in an oil bath held at 90–97°. The clear yellow solution solidified upon cooling (ten minutes) to a yellow solid, which was crystallized from methyl alcohol to give clear yellow crystals; m.p. 128–9° (1.5 g.).

Thermal decomposition of 3-benzoyl-4-phenyl-Δ^2-pyrazoline (VII). Preparation of dypnone (VIII).—The pyrazoline (VII) (1.5 g.) was placed in a small test-tube, a thermometer was immersed in the solid, which was heated in an oil bath. Gas evolution began at a temperature of 178° and became brisk at 200°. The temperature was held at about 200° as long as any evolution of gas was apparent (1.5 hours). The liquid was a clear orange-red in color. Vacuum distillation yielded 1.0 g. of clear yellow liquid; 197–200°/13 mm.

Oxime.—A few drops of the yellow oil was dissolved in 15 cc. of ethyl alcohol and boiled under reflux for five hours with an excess of hydroxylamine hydrochloride; the solution was then diluted with water and cooled. The solid product which separated was crystallized twice from dilute alcohol, when it melted at 126–8° (softened at 120°). This sample did not depress the melting point of a known sample of dypnone oxime; 126–30° (softened at 121°).

A similar result was obtained with some of the lower melting pyrazoline (VI). Two grams of impure material (m.p. 87–90°) was placed in a test-tube, a thermometer was immersed in the solid, and the tube was heated gently. There was some sign of reaction at about 100°, and at 130–40° a vigorous reaction took place, the temperature rising to 190–200° without further heating. The material was boiled gently for a few minutes (temperature 240–50°), then allowed to cool. The orange-red oil could not be solidified, and was vacuum-distilled; a yellow viscous oil passing over at 185–90° under 13 mm. pressure. The oil did not contain nitrogen.

Thermal decomposition of 3-benzoyl-4-phenyl-Δ^1-pyrazoline (VI). Preparation of 3-benzoyl-4-phenyl-pyrazole (X).—A portion of the pyrazoline (VI) which had started to decompose upon standing for four months was placed in a small sausage-type flask and distilled at atmospheric pressure. The distillate was a yellow oil which solidified upon cooling. The material was taken up in boiling chloroform, and filtered from a small amount of undissolved material (m.p. 215–220°), petroleum ether was added, the solution was cooled, and the colorless, fluffy precipitate was separated by filtration; m.p. 170–73°. Concentration of the filtrate gave a further quantity of colorless material; m.p. 191–193°. After crystallization from ethyl acetate-petroleum ether and ethyl alcohol, the melting point was 193–4°. The two other products were not investigated further.

Anal. (substance of m.p. 193–4°) Calc'd for $C_{16}H_{12}N_2O$: C, 77.42; H, 4.84
Found: C, 76.50, 76.99; H, 5.16, 5.14.

A small amount of colorless material of the same melting point had been noticed previously in the thermal decomposition of the isomeric 3-benzoyl-4-phenyl-Δ^2-pyrazoline (VII).

Action of bromine on 3-benzoyl-4-phenyl-Δ^2-pyrazoline (VII). Preparation of 3-benzoyl-4-phenyl-pyrazole (X).—A small amount of the pyrazoline (VII) was dissolved in carbon disulfide and a solution of bromine in carbon disulfide was added slowly. Two products were obtained: bright yellow crystals, which after crystallization from methyl alcohol, melted (d.) at 120–22° (not investigated further), and a smaller amount of colorless material, m.p. 193–4° after crystallization from ethyl acetate-petroleum ether and dilute ethyl alcohol. The melting point of a mixture with the thermal decomposition product having the same melting point, showed no depression.

SUMMARY

1. Diazomethane has been added to benzalacetophenone, giving two isomeric pyrazolines which are represented as 3-benzoyl-4-phenyl-Δ^1- and -Δ^2-pyrazolines.

2. The lower-melting compound may be changed into its isomer by heating to slightly above its melting point.

3. Thermal decomposition of these pyrazolines gives a number of substances, among which are dypnone and a nitrogen-containing compound represented as 3-benzoyl-4-phenyl-pyrazole.

4. The action of bromine on the higher-melting pyrazoline gives the same pyrazole as is obtained in the thermal decomposition.